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GB 1537379

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(58) Field of search

C1A

C3K

Selected US specifications from IPC sub-class C09C

(54) **Process for modifying the surface characteristics of carbon black**

(57) The surface characteristics of a furnace carbon black having a nitrogen surface area greater than 140 m²/g, are modified by treating the black with an organic adsorbate (eg. an *n*-alkane, *n*-alkane amine, *n*-alkane halide or *n*-alkane alcohol) having a molecular structure including a linear chain having at least four carbon atoms at a loading ranging from 1 to 2 percent by weight, whereby carbon black pores can be filled to effectively block adverse moisture absorption.

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SPECIFICATION

Process for modifying the surface characteristics of carbon black and carbon black produced thereby

- 5 Carbon black is produced by the thermal decomposition of hydrocarbons at very high temperatures. The blacks so formed are composed of essentially elemental carbon in the form of aggregated particles of colloidal dimensions and high surface area. All carbon blacks, regardless of the method of manufacture or raw materials used in their production, possess many similar properties. The distinction between the various types or grades of carbon blacks is one of degree rather than kind, and is based on such characteristics as
- 10 particle size, surface area, chemical composition of the particle surface, and extent of particle to particle association.
- The carbon black particles generally are porous and feature both external and internal surface areas. Specific surface areas, typically evaluated by adsorption techniques, commonly are used to identify and classify the blacks. Various product performance characteristics have been attributed to the internal and/or
- 15 external surface areas of the carbon blacks incorporated therein.
- Carbon black is a widely used ingredient for imparting conductivity to polymer systems. One such application is in anti-static compounds, such as for sheeting, belting, hoses, and molded goods, in order to minimize static build-up and explosion hazards in environments such as mines, hospitals, and other areas where solvent vapors or oxidants may collect. In the wire and cable industry, conductive carbon black compounds are utilized as metal conductor strand shielding in high voltage cables.
- 20 When carbon black is incorporated into polymer systems, however, the compound moisture absorption (CMA), the amount of moisture absorbed by the compound, may increase. The increase in CMA in conductive polymers can contribute to at least two significant problems. Firstly, the moisture absorbed in the compound can be vaporized during the extruding operations where temperatures can exceed 100°C (373°K). This vaporization results in "blow-holes" on the surface of the extrudate, which are a potential source of dielectric
- 25 weakness. Secondly, the moisture absorbed in the compound can itself initiate dielectric breakdown by a process referred to in the art as "treeing". (The descriptive term "treeing" is derived from the shape of dielectric breakdown pathways as observed by microscopic examination.)
- In particular, when certain conductive blacks are compounded into polymeric materials, the increase in
- 30 CMA has been found to be primarily attributable to the microporosity of the carbon black. Now, according to the present invention, a process has been discovered whereby the microporosity of a carbon black can be selectively modified. The carbon black is treated with an organic adsorbate which is adsorbed by the black and effectively blocks micropores in a specific size range, while not adversely affecting other compound properties.
- 35 Applicant has determined that by treating a carbon black with an adsorbate, featuring select molecular dimensions, pores of a select diameter range can be filled and thereby effectively block adverse moisture absorption. It was found that the molecules of select adsorbate become firmly bound to the carbon black and do not become liberated under normal handling, storage, or use conditions. Theory suggests that the overlapping potential fields present in such small pores bind the adsorbate molecules with relatively high energies making it difficult to displace the molecule from the micropore.
- 40 The treatment according to the present invention may be effectively applied to any grade of carbon black having a surface micro-structure featuring a significant portion of micropores in the size range penetrable by molecules of water. The black may be in pelleted or fluffy form. Accordingly, the treatment has been found to produce favorable results in modifying high surface area furnace blacks (having a nitrogen surface area
- 45 $[N_2SA]$ greater than about 140 m²/g), since these blacks appear to feature a surface micro-structure with a significant portion of micropores in the specified size range. Effective results have been accomplished in treating preferred furnace blacks having a N_2SA ranging from about 200 m²/g to about 260 m²/g.
- The adsorbate of the present invention may be any organic molecule including a linear chain having at least four carbon atoms, such as alkanes and substituted alkanes (amines, halides, alcohols, and the like) and
- 50 mixtures thereof. Typical materials include n-octane, n-amino octane, n-hexanol, n-bromo octane, n-chloro octane, 4 methyl heptane, 2-5 dimethyl heptane, 2-3-4 trimethyl pentane, 2-2-4 trimethyl pentane, hexamethyl ethane, n-nonane, n-decane, n-dodecane, n-hexadecane, 1-3 dichloro propane, and the like. For reasons of efficiency and permanence of treatment during heat processing, adsorbates featuring a linear chain of at least ten carbon atoms are preferred. Particularly preferred are n-alkanes, C₁₀-C₁₆, which feature
- 55 thermal stability to above about 250°C (523°K).
- The manner in which the adsorbate is applied to the carbon black is not critical. Typically, the treatment simply consists of mixing the chosen amount of adsorbate with the black in a suitable vessel and then agitating the black to ensure adsorbate impregnation of the black surface. Excess or unadsorbed adsorbate can be removed by drying the treated black at moderate temperatures, typically ranging from about 100° to
- 60 200°C (373 to 473°K). Treatment of the black also may conveniently be incorporated into various process steps during manufacture or utility of the carbon black. For example, a suitable adsorbate may be injected into the process stream of a carbon black reactor prior to collection of the black, or, the adsorbate may be introduced during a compounding operation as a black is being blended with a polymer.
- The optimum amount of adsorbate to be used depends on the carbon black to be treated, its surface area,
- 65 and the percentage of that surface area consisting of micropores in the size range effectively blocked by the

adsorbates of the present invention. When treating conductive carbon black, effective results have been accomplished using about 0.5 to about 5 percent by weight adsorbate; about 1.0 to about 2.0 percent adsorbate is particularly preferred.

The following examples are provided to further illustrate the invention. The examples are intended to be illustrative in nature and are not to be construed as limiting the scope of the invention.

Test procedures

An amount of carbon black was weighed into a glass jar and a measured percent by weight of adsorbate then was added to the black. The jar was sealed with a lid and the contents were thoroughly mixed by rolling the jar for about one to five minutes (60 to 300 seconds). After loosening the lid, the jar and its contents were then placed in an oven to dry.

In order to evaluate the performance characteristics of the blacks in imparting compound moisture adsorption and volume resistivity properties, the blacks were compounded with a suitable resin. For purposes of illustration, an ethylene/ethyl acrylate (EEA) was used as the resin in the following examples. The compound to be tested was prepared by incorporating the desired amount of black into the resin, on a weight percent basis. The blacks were compounded, at specified loadings, into the EEA using a Brabender mixer running at 60 RPM with circulating oil at 110°C (383°K) for nine minutes (540 seconds). The resulting compound was sheeted on a cold two-roll mill and formed into sheets for the subsequent testing.

In order to determine CMA, sheets of the various ethylene/ethyl acrylate (EEA) compounds were diced or cut into pellets to yield suitable granulated test samples. A three gram sample of the granulated compound was weighed into a glass crucible of known weight and dried at 60°C ± 3° (333°K) and 1/3 atmosphere (3.4 × 10⁴ Pa) for two hours (7200 seconds) to remove moisture from the compound. After cooling in a desiccator, the weight was obtained to the nearest tenth of a milligram. The compound then was placed into a desiccator maintained at conditions of room temperature (70 ± 2°F [294°K]) and 79 percent relative humidity (R.H.) for 48 hours (1.728 × 10⁵ seconds). The compound then was weighed after 30 minutes (1800 seconds) and periodically at 24 hour (8.64 × 10⁴ seconds) intervals until constant weight (0.03 percent increase in CMA) was achieved. The equilibrium moisture absorptoin was calculated as a weight percentage of the compound using the following formula:

$$\text{CMA (wt \%)} = \frac{(C + S) - (C + \text{DS}) - B}{(C + \text{DS}) - (\text{TC})} \times 100$$

wherein

C + S = final weight container + sample
C + DS = weight container + dry sample
TC = tare weight glass crucible
B = change in weight blank container

Volume resistivity of a material is the ratio of the potential gradient parallel to the current in the material to the current density. Volume resistivity is measured in ohms centimeter; it is the reciprocal of volume conductivity. In order to determine the volume resistivity of plastic compounds containing carbon black, samples were prepared by molding standard 80 mil tensile plaques from the millsheets and 2" × 6" (5.1 × 15.2 cm) electrical test specimens were cut out of the tensile plaques. Each specimen was coated with a silver paint (silver conductive coating in ethyl alcohol) to produce a one-half inch (1.27 cm) wide silver electrode at each end. The specimens were placed in a sample holder (between 8 × 6 [20.3 × 15.2 cm] glass plates arranged crosswise to each other such that the edge of the top plate is evenly lined with the edge of the specimen) and the electrodes attached to a Leeds and Northrup test set (#5035) consisting of a Wheatstone Bridge and Galvanometer. The voltage impressed on the test specimens was approximately 4.5 volts. The DC resistances across the length of the sample were measured and converted to Volume Resistivity in ohm-cm using the following formula:

$$\text{Volume Resist (ohm-cm)} = \frac{2 \times T \times (2.54) \times R}{5 \times (2.54)}$$

wherein

T = thickness of sample (inches)
R = resistance (ohms)
2.54 = conversion constant (in. → cm)
5 = distance constant (inches) - measure of the distance between the two one-half inch silver electrodes painted on each end of the test specimen

The resistance of the specimen was measured in an oven maintained at 90°C (363°K). In doing so, the resistance initially was measured after three minutes (180 seconds) at 90°C (363°K) with subsequent readings being taken at two minute (120 second) intervals for the next 30 minutes (1800 seconds). After 30 minutes (1800 seconds) readings were taken every five minutes (300 seconds) until the specimen had been in the 90°C (363°K) oven for a total of 60 minutes (3600 seconds). The value for the resistance of the specimen at 90°C (363°K) was fixed on a plot as the point at which the readings became constant.

Nitrogen surface area (N_2SA) of the carbon black samples was determined in accordance with ASTM Test Method D3037-76, Method C, and is expressed in terms of square meters per gram (m^2/g).

The table below list representative results obtained using a selection of blacks and adsorbates.

10 Tables I and II list results with two different carbon black samples and using varying amounts of two adsorbates. 10

The data shown in Table III indicates that treatment with homologs of n-alkanes demonstrate comparable beneficial results. Increasing the chain length of the adsorbate has the benefit of offering higher atmospheric boiling points and higher temperature stability against desorption.

15 Table IV reports the effects of treatment using various isomers of octane. The adsorbate molecules all feature the same molecular formula but exhibit increasing degrees of branching moving from the top to the bottom of the table. While treatment with all of the adsorbates demonstrated beneficial results, linear molecules were most effective. 15

20 Table V lists treatment results from using various adsorbates, including both substituted and unsubstituted alkanes. The amines and alcohols appear to have a slight affinity for water which is not present for the halogenated and unsubstituted alkanes. 20

Table VI reports the results wherein carbon blacks of varying surface areas were treated. The example employing a low surface area black (about 50 m^2/gm) evidenced no effect when treated pursuant to the present invention.

25 Table VII reports results wherein carbon blacks of varying surface areas were treated with varying amounts of n-decane adsorbate. 25

Table I

30 Compound: Carbon Black* (36% Loading) in EEA 30

| Adsorbate (wt%) | Treatment Conditions | CMA (wt%) | Volume Resistivity | |
|--------------------|-------------------------|--------------|-----------------------|------|
| | | | 25°C | 90°C |
| CONTROL | 150°C/60 min | 0.66 | 3.12 | 13.5 |
| 3% n-octane | | 0.29 | 2.76 | 10.8 |
| CONTROL | 150°C/60 min | 0.63 | 2.75 | 11.5 |
| 1.5% n-octane | | 0.29 | 2.59 | 10.3 |

*The carbon black was VULCAN XC-72 (ASTM-N-472), a conductive carbon black available from Cabot Corporation, having a nitrogen surface area of about 215-260 m^2/g .

Table II

45 COMPOUND: Carbon Black* (36% Loading) in EEA 45

| Adsorbate (wt%) | Treatment Conditions | CMA (wt%) | Volume Resistivity | | |
|--------------------|-------------------------|--------------|-----------------------|------|----|
| | | | 25°C | 90°C | |
| 50 CONTROL | 150°C/60 min | 2.45 | 1.9 | 5.1 | 50 |
| 3% n-octane | " | 0.92 | 2.2 | 5.1 | |
| 4.5% n-octane | " | 0.43 | 2.1 | 6.0 | |
| 55 CONTROL | | 2.49 | 1.9 | 5.6 | 55 |
| 3% n-octane | " | 1.08 | 1.6 | 3.9 | |
| 4.5% n-octane | " | 0.55 | 2.1 | 6.0 | |

*The carbon black used had a nitrogen surface area of about 610 m^2/g .

Table III

COMPOUND: Carbon Black* (36% Loading) in EEA

| 5 | Adsorbate (wt%) | Treatment Conditions | CMA (wt%) | Volume Resistivity | | 5 |
|----|---------------------|-------------------------|--------------|-----------------------|------|----|
| | | | | 25°C | 90°C | |
| | CONTROL | | 0.56 | 3.3 | 10.4 | |
| 10 | 1 1/2% n-octane | 200°C/12 hrs | 0.22 | 2.8 | 9.1 | 10 |
| | 1 1/2% n-decane | " | 0.23 | 2.9 | 8.7 | |
| | 1 1/2% n-dodecane | " | 0.24 | 3.2 | 10.1 | |
| | 1 1/2% n-hexadecane | " | 0.24 | 3.2 | 10.3 | |

15 Table IV

COMPOUND: Carbon Black* (36% Loading) in EEA

| 20 | Adsorbate (wt%) | Treatment Conditions | CMA (wt%) | Volume Resistivity | | 20 |
|----|------------------------------|-------------------------|--------------|-----------------------|------|----|
| | | | | 25°C | 90°C | |
| | CONTROL | 200°C/12 hrs | 0.66 | 2.9 | 9.6 | |
| | 1.5% n-octane | " | 0.20 | 2.8 | 9.1 | |
| | 1.5% 4 methyl heptane | " | 0.28 | 3.1 | 11.5 | |
| 25 | 1.5% 2-5 dimethyl heptane | " | 0.28 | 3.3 | 10.1 | 25 |
| | 1.5% 2-3-4 trimethyl pentane | " | 0.35 | 3.2 | 10.5 | |
| | 1.5% 2-2-4 trimethyl pentane | " | 0.38 | 2.7 | 8.5 | |
| | 1.5% hexamethyl ethane | " | 0.44 | 5.4 | 25.5 | |

30 *The carbon black used was VULCAN XC-72 (ASTM-N-472), a conductive carbon black available from Cabot Corporation, having a nitrogen surface area of about 215-260 m²/g.

Table V

35 COMPOUND: Carbon Black* (36% Loading) in EEA

| 40 | Adsorbate (wt%) | Treatment Conditions | CMA (wt%) | Volume Resistivity | | 40 |
|----|--------------------------|-------------------------|--------------|-----------------------|------|----|
| | | | | 25°C | 90°C | |
| | CONTROL | | 0.65 | 2.8 | 12.2 | |
| | 1% n-octane | 150°C/50 min | 0.29 | 2.6 | 10.3 | |
| | 3% n-amino octane | " | 0.34 | 3.6 | 17.4 | |
| | 2% n-hexanol | 150°C/12 hrs | 0.44 | 3.0 | 14.0 | |
| 45 | CONTROL | | 0.77 | 4.5 | 31.9 | 45 |
| | 2% n-octane | 110°C/60 min | 0.36 | 3.7 | 17.1 | |
| | 2% n-decane | " | 0.32 | 3.7 | 18.1 | |
| | 2% n-bromo octane | " | 0.38 | 3.9 | 19.5 | |
| | 2% n-chloro octane | " | 0.33 | 3.3 | 14.6 | |
| 50 | 1.5% 1-3 dichloropropane | " | 0.30 | 2.8 | 9.3 | 50 |

*The carbon black used was VULCAN XC-72 (ASTM-N-472), a conductive carbon black available from Cabot Corporation, having a nitrogen surface area of about 215-260 m²/g.

Table VI

COMPOUND: Carbon Black (36% Loading) in EEA

| 5 | Adsorbate (wt%) | N ₂ SA (m ² /gm) | Loading (wt%) | Treatment Conditions | CMA (wt%) | Volume Resistivity | | 5 |
|----|-----------------------------|---|------------------|-------------------------|--------------|-----------------------|------|----|
| | | | | | | 25°C | 90°C | |
| | CONTROL A | 50 | 36 | 150°C/60 min | 0.38 | 4.1 | 74 | |
| 10 | 1.5% Norpar 12 ¹ | 36 | | " | 0.38 | 4.2 | 76 | 10 |
| | CONTROL B | 138 | 36 | " | 0.44 | 3.5 | 21 | |
| | 1.5% Norpar 12 | | 36 | " | 0.27 | 3.9 | 21 | |
| 15 | CONTROL C | 224 | 36 | " | 0.78 | 2.6 | 11 | 15 |
| | 1.5% Norpar 12 | | 36 | " | 0.46 | 2.6 | 9 | |
| | 1.5% Norpar 12 ² | 36 | | N/A | 0.52 | 2.2 | 8 | |
| | CONTROL D | 635 | 14 | 150°C/60 min | 1.03 | 45 | 146 | |
| 20 | 4.5% n-nonane | | 14 | " | 0.22 | 56 | 192 | 20 |
| | CONTROL E | 810 | 14 | " | 0.45 | 9 | 26 | |
| | 3% n-decane | | 14 | " | 0.26 | 11 | 27 | |
| 25 | CONTROL F | 1727 | 12 | " | 0.33 | 16 | 19 | 25 |
| | 3% Norpar 12 | | 12 | " | 0.11 | 15 | 18 | |

(1) Norpar 12 is a mixture of n-alkanes having an average of 12 carbons (commercially available from Exxon Company USA).

30 (2) In this example, the adsorbate was introduced during the carbon black/EEA compounding operation. 30

Table VII

COMPOUND: Carbon Black (36% Loading) in EEA

| 35 | Adsorbate (wt%) | N ₂ SA (m ² /gm) | Loading (wt%) | Treatment Conditions | CMA (wt%) | Volume Resistivity | | 35 |
|----|--------------------|---|------------------|-------------------------|--------------|-----------------------|--|----|
| | | | | | | 90°C | | |
| 40 | CONTROL 1 | 142 | 36 | 150°C/60 min | 0.49 | 34.2 | | 40 |
| | .75% n-decane | | 36 | " | 0.37 | 34.7 | | |
| | CONTROL 2 | 235 | 36 | " | 0.78 | 16.7 | | |
| | 1.5% n-decane | | 36 | " | 0.39 | 13.0 | | |
| 45 | CONTROL 3 | 1052 | 14 | " | 0.45 | 26.0 | | 45 |
| | 3% n-decane | | 14 | " | 0.26 | 26.5 | | |
| | CONTROL 4 | 1322 | 14 | " | 0.63 | 19.2 | | |
| 50 | 3% n-decane | | 14 | " | 0.38 | 20.6 | | 50 |

CLAIMS

1. A method for modifying the surface characteristics of a furnace carbon black having a nitrogen surface area greater than 140m²/g comprising treating the surface of said carbon black with an organic adsorbate having a molecular structure including a linear chain having at least four carbon atoms. 55
2. The method of claim 1 wherein said carbon black has a nitrogen surface area ranging from 200 to 260 m²/g.
3. The method of claim 1 wherein said carbon black is treated with an organic adsorbate comprising an n-alkane, n-alkane amine, n-alkane halide or n-alkane alcohol. 60
4. The method of claim 3 wherein the organic adsorbate is an n-alkane having 10 to 16 carbon atoms, or mixture thereof.
5. The method of claim 4 wherein said carbon black having nitrogen surface area ranging from 200 to 260 m²/g is treated with adsorbate at a loading ranging from 1 to 2 percent by weight.
- 65 6. A modified carbon black obtained by treating a furnace carbon black having a nitrogen surface area 65

greater than 140 m²/g with an organic adsorbate including a linear chain having at least four carbon atoms.

7. The carbon black of claim 6 wherein the organic adsorbate is an n-alkane amine, n-alkane, n-alkane halide or n-alkane alcohol.

8. The carbon black of claim 6 wherein the organic adsorbate is an n-alkane having 10 to 16 carbon atoms or mixtures thereof. 5

9. The carbon black of claim 6 obtained by treating a carbon black having a nitrogen surface area ranging from 200 to 260 m²/g.

10. The carbon black of claim 8 obtained by treating a furnace carbon black having a nitrogen surface area ranging from 200 to 260 m²/g with adsorbate at a loading ranging from 1 to 2 percent by weight.

10 11. A method for modifying the surface characteristics of a furnace carbon black as claimed in claim 1 and substantially as herein described with reference to the Examples. 10

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